Environmental Fate of Carbaryl

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I. Introduction

Carbaryl (1-naphthyl-*N*-methyl carbamate; Fig. 1) is a carbamate insecticide introduced in 1956 by Union Carbide Corporation. The insecticide is used worldwide and is a substitute for some organochlorine pesticides (Ribera et al., 2001). Carbaryl controls a broad spectrum of insects on more than 120 different crops (Ware, 2000). It has also been used to prevent bark beetle attacks in pine trees (Hastings et al., 2001) and as a general garden insecticide (Ware, 2000). In 2004, approximately 110,000 kg of the insecticide was applied in California alone (CDPR, 2004). Annual use in the U.S. is reported to be 4.5-6.8 million kg (Cox, 1993). Several trade names are associated with carbaryl; the most common being Sevin[®]. Active ingredient (a.i.) use rates for carbaryl range from 0.57-4.5 kg/ha (Rajagopal et al., 1984). It is available in the form of a wettable powder, pellets, granules, suspensions, and solutions. The insecticide is the second most widely detected insecticide in surface waters in the U.S. (Martin et al., 2003).

Fig. 1. Chemical structure of carbaryl.

II. Chemistry

Carbaryl, like most carbamates, inhibits the enzyme that degrades acetylcholine - acetylcholinesterase. Inhibition of this enzyme promotes the buildup of acetylcholine at synapses resulting in uncontrolled movement, paralysis, convulsions, and possible death (Tomlin, 2000).

The physical chemical properties of carbaryl are listed in Table 1. Carbaryl is a low molecular weight compound that is moderately soluble in water and does not readily volatilize. The compound is not compatible with alkaline materials such as lime (Tomlin, 2000).

Table 1. Physical-chemical properties of carbaryl.

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Pure physical state ^a	Colorless or tan crystal
Chemistry Abstracts Service registry number (CAS #) b	63-25-2
Molecular weight (g/mol) ^a	201.2
Molecular formula a	$C_{12}H_{11}NO_2$
Melting point (°C) ^a	142
Vapor pressure (mPa at 23.5°C) ^a	0.041
Octanol-water partition coefficient (log K_{ow}) ^a	2.36
Density (20°C) ^a	1.23
Henry's law constant (atm m ³ g/mol at 25°C) ^a	2.74×10^{-9}
Organic-carbon normalized partition coefficient $(K_{oc})^{b}$	290
λ_{\max} (nm) ^c	280
Water solubility (mg/L) 20°C a	120
25°C ^d	104
40°C ^e	40

^a Tomlin, 2003; ^b Phillips and Bode, 2004 ^c Sheng et al., 2001; ^d Arroyo et al., 2004; ^e Meister, 2001.

III. Chemodynamics

A. Air

The low vapor pressure measured for carbaryl makes the possibility of volatilization unlikely (Table 1). Additionally, its low Henry's law constant suggests that it will not volatilize from aqueous solutions (Table 1). However, carbaryl could become airborne from binding to particulates or as a spray drift immediately following application. Drift monitoring from aerial spraying of carbaryl at a rate of 2250 g a.i./ha on a Vermont apple orchard revealed concentrations of 0.70-7.20 µg/plate (1 mm thick Teflon sheet covered the 15 cm diameter petri plate), which corresponds to 0.4-4.1 g a.i./ha, as far out as 305 meters with 8-12 km/h winds (Currier et al. ,1982). Higher concentrations (481 µg/plate) were observed at 76 meters

downwind and 12 meters upwind (45.9 μ g/plate) in the same study. But, the study noted that all detections decayed to relatively low concentrations within 2 hours after application (< 2 μ g/m³; Currier et al., 1982). Airborne carbaryl degrades after reaction with hydroxyl radicals in the atmosphere (Kao, 1994). Sun et al. (2005) determined the reaction rate constant for carbaryl hydroxyl radical reactions at 3.3×10^{-11} cm³/second.

Low drift concentrations were reported in a California study with concentrations up to $1.12~\mu g/m^3$ in the air after ground spraying to control the glassy-winged sharpshooter, *Homalodisca coagulate* (Walters et al., 2003). Although below the adverse health effect concentration (51.7 $\mu g/m^3$), the study indicated that the insecticide was present in the air up to 47 hours after application (Walters et al., 2003). Shehata et al. (1984) also reported atmospheric concentrations that ranged from 0.0035 to 0.107 $\mu g/m^3$ in a Maine forest treated with carbaryl to control the spruce budworm.

In eastern France, air concentration measurements for carbaryl at remote (non-populated), rural (population = 80,000), and urban (population = 300,000) sites were on average 280, 348, and 577 pg/m³ with highest detections at 1800, 696, and 1420 pg/m³, respectively (Sanusi et al., 2000). The increased urban and rural carbaryl concentrations were primarily due to local agricultural use (Sanusi et al., 2000). Similar concentrations were observed in 1995 at three urban and agricultural sites along the Mississippi River (Foreman et al., 2000). However, carbaryl was detected more frequently in urban sites than agricultural sites in Mississippi and lowa and possibly reflective of its growing domestic use (Foreman et al., 2000).

B. Water

Carbaryl is moderately soluble in water and its solubility increases with increasing temperature and amount of organic solvents. Detections of carbaryl have been found in surface waters of 42 U.S. states at low concentrations (µg/L). In many states, detections were found in both agriculture and urban environments (Table 2). Several state reported higher frequency of detections in urban than in agricultural environment. In California, detections in urban environments are less than in agricultural areas (Table 2). Carbaryl ranked 8th nationally among pesticides for outdoor home-and-garden use in 1992 (Whitmore et al., 1992), and one of four insecticides most commonly detected in urban streams in 2001 (Gilliom et al., 2007). Agricultural inputs of carbaryl to water systems have also been reported. In Florida, Wilson et al. (2006) detected carbaryl in eight of 457 samples collected from Ten Mile Creek located in an agricultural watershed at concentrations that ranged from 0.33-0.95 µg/L. Lower concentrations of carbaryl (10-100 ng/L) were detected in the Pinios River in Greece with seasonal use of the insecticide in the Thessaly agricultural area (Fytianos et al., 2006). Higher concentrations have been detected in several locations after carbaryl was used across central California to control the newly introduced glassy-winged sharpshooter pest, *Homalodisca coagulate*. For instance, 6.94 μg/L in a goldfish pond and 1737 μg/L in rain runoff in a drain were detected adjacent to where carbaryl was sprayed (Walters et al., 2003).

Groundwater detections are also reported by LaFleur (1967) who found the presence of carbaryl within two months after application to Congaree soil (well drained loamy soil on river bed) with detections continuing up to eight months. Table 2 shows that New Jersey had the highest number of carbaryl detections in groundwater across all land use types. Several other states also had groundwater detections mainly in urban and mixed-use areas.

Table 2. Detection of carbaryl in U.S. surface and ground water according to the U.S. Geological Survey * .

			baryl		
State	Type of Land	Surface Water	Ground Water	Concentration	
	use	Detections	Detections	Range (µg/L)	
	Urban	61	1		
Alabama	Agriculture	19	2	0.002-0.422	
	Mixed	41	1		
	Urban	166	-		
California	Agriculture	251	1	0.0005-5.20	
	Mixed	432	1		
Alaska	Urban	20	-	0.002-0.332	
	Urban	190	-		
Colorado	Agriculture	27	-	0.0005-16.5	
•	Mixed	126	3		
	Urban	39	-		
Florida	Agriculture	21	-	0.003-0.441	
	Mixed	39	-	***	
	Urban	208	1		
Georgia	Agriculture	20	-	0.001-1.90	
	Mixed	177	_		
Hawaii	Mixed	8	-	0.007-0.370	
	Urban	9	_		
	Urban	119	-		
Indiana	Agriculture	69	_	0.001-0.460	
•	Mixed	62	_		
	Urban	122	5	0.001-1.50	
New Jersey	Agriculture	24	5		
	Mixed	89	9	****	
	Urban	119	<u>-</u>		
Pennsylvania	Agriculture	82	1	0.001-2.41	
T CITIES y I V CITICA	Mixed	82	9	****	
	Urban	164	7		
Texas	Agriculture	13	_	0.001-5.18	
	Mixed	138	4		
Virginia	Urban	165	2		
	Agriculture	14	-	0.002-2.0	
	Mixed	45	3		
Washington	Urban	46			
	Agriculture	267	1	0.001-33.5	
	Mixed	106	2	U.UU1 JJ.J	
	Urban	27			
Wisconsin					
Wisconsin	Agriculture	8	_	0.002-0.267	

^{*} U.S.G.S., 2007.

Organic compound sorption to soils, in general, may prevent surface and groundwater contamination and in this section the sorptive processes of carbaryl are reviewed. Carbaryl sorption to soil is rapid at 0.5 hours (Ahmad et al., 2001a) and 3 hours (Jana and Das, 1997) but persistent (from two to 16 weeks) with a $t_{1/2}$ of ~8 days for concentrations ranging from 1-14 mg/L (Rajagopal et al., 1984). Carbaryl has been found to adsorb more readily to acidic soil (Rajagopal et al., 1984). Both mineral and organic matter in soils has been found to contribute to carbaryl sorption. The mineral interactions are clearly reported in several recent studies. For instance, Sheng et al. (2001) found that potassium (K) saturated smectite clay (a non-ionic, expandable, hydrophilic clay) is a better sorbent for carbaryl than soil organic matter (SOM); the distribution coefficient (K_d) for carbaryl was five times greater in clay (235) than SOM rich soil (muck; 54.2). Sheng et al. (2001) estimated that K saturated clay contributes approximately 35 times more to carbaryl retention than a soil with 2% SOM. De Oliveira et al. (2005) found that its sorption is dependent on the surface charge density and is site-specific. For example, the amount of carbaryl sorbed was strongly dependent on the presence of specific exchangeable cations and followed the order of Ba \sim Cs \sim Ca > Mg \sim K > Na \sim Li. The carbonyl group in carbaryl was found to directly interact with the exchangeable cations; Mg²⁺ and Na⁺ interacted strongly with the partial negative charge of the double-bonded oxygen atom on the insecticide (De Oliveira et al., 2005). A positive correlation between carbaryl sorption with surface area, cation exchange capacity (CEC), and free Al₂O₃ content in Ultisol and Inceptisol soils was made by Jana and Das (1997). Sorption isotherms of carbaryl sorption to Indian soils followed reversible S-shaped curves which suggest multilayer adsorption on the sorbent surface (Jana and Das, 1997).

Organic matter is another contributor to sequestering carbaryl in soils. For example, carbaryl movement through soil was found to be a function of SOM content; \sim 52% carbaryl was leached in ten rinses from organic rich soil while it took only one rinse to leach the same amount from a sandy soil (Sharom et al., 1980). The positive contribution of SOM to carbaryl sorption is evident in Table 3 where the sorption capacity (K_f) increases with SOM content in Indian soils (Jana and Das, 1997).

Table 3. The relationship between soil organic matter (SOM) and the sorption capacity (K_f) in four different soils from India (Jana and Das, 1997).

Soil	SOM (%)	$K_{\rm f}(\mu g/g)/(\mu g/mL)$
Ultisol 1	0.40	0.308
Inceptisol 2	1.10	1.916
Ultisol 2	1.16	2.175
Inceptisol 1	1.70	2.490

Table 4 summarizes a large data set on the sorption of carbaryl to soils from four countries (Ahmad et al., 2001a). While the table shows that organic carbon influences the sorption (K_d) of carbaryl, a positive correlation between the two was not observed by Ahmad et al. (2001a). However, in a similar study by the same group (Ahmad et al., 2001b), a positive, highly significant, correlation of organic carbon normalized sorption capacity (K_{oc}) and aromatic content of SOM was observed. Similar K_d values to those presented in Table 4 are reported elsewhere (Bondarenko and Gan, 2004) and indicate the sorption of carbaryl to soils is not very significant.

Sorption processes are predicted to be highly reversible for carbaryl since the binding is proposed to be nonspecific sorptive binding unlike chemisorption (Rajagopal et al., 1984). This, along with reported low K_d values, indicate that soils do not have a significant potential to stop carbaryl movement, with time, into water systems and other environmental fate processes (i.e., abiotic or biotic degradation) may play an important role in its dissipation.

Table 4. Distribution coefficients (K_d) for carbaryl in several soils with different organic carbon (OC) content.

Soil	OC (g/kg)	K _d	Sand:Silt:Clay (%)
Pakistan 2 ^a	2.79	0.99	22:60:18
Australian 2 ^a	3.0	0.19	92:5:3
United Kingdom 2 ^a	8.9	1.09	10:67:23
Pakistan 1 a	13.82	59.67	22:51:27
Australian 1 a	58	23.02	63:16:21
United Kingdom 1 ^a	83.8	8.80	18:39:43
California 1 b	-	43.4	-
California 2 ^b	-	47.7	-

^a Ahmad et al., 2001a; ^b California 1 and 2 represent sediment from San Diego Creek and Bonita Creek in California, USA (Bondarenko and Gan, 2004).

IV. Degradation

A. Abiotic

1. Hydrolysis

Carbaryl is effectively hydrolyzed in water and undergoes 50% loss at 20°C and pH 8 in 4 days (Rajagopal et al., 1984). Earlier studies reported similar degradation times: 6 days in flowing canal water (Osman and Belal, 1980) and one week in river water (Eichelberger and Lichtenberg, 1971). These and other investigators (Ghauch et al., 2001) showed that hydrolysis of the compound increases with elevated temperature. Hydrolytic degradation was shown to be mediated by hydroxyl radical oxidation (Fig. 2; Wang and Lemley, 2002). 1-naphthol was identified as the primary degradation product of carbaryl (Osman and Belal, 1980).

2. Photolysis

Carbaryl was photolyzed into 1,2-naphthoquione, 1,4-naphthaoquinone, 2-hydroxy-1,4-naphthoquinone, and 7-hydroxy-1,4-naphthoquinone (Brahimia and Richard, 2003). Carbaryl in water produced naphthoxyl radicals and demonstrated the hemolytic cleavage of the carbonoxygen bonds. In oxygen rich water, however, solvated electrons could be transformed into

super-oxide anions that can recombine with radical cations or with 1-naphthoxyl radicals. Both reactions are expected to produce naphthoquinones after reduction (Brahmia and Richard, 2003).

Fig. 2. The degradation pathways of carbaryl (A) by hydroxyl radical attack (C and E) showing the degradation products; 1-naphthol (B), 1,4-naphthoquinone (D), and (F) (phthalic acid-*O*-)yl *N*-methylcarbamate (Wang and Lemley, 2002).

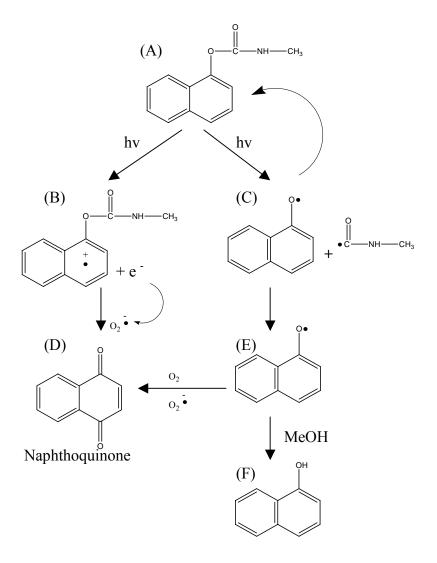


Fig. 3. Proposed (Brahmia and Richard, 2003) photolytic degradation pathway for carbaryl (A). The parent compound is distributed into radicals (B and C) via photolytic processes. 1-naphthoxyl (C) may then react with oxygen to yield naphthoquionone (D) or 1-naphthol (F). 2003). Proposed photolysis is shown (Fig. 3). Photo-conversion of carbaryl to 1-naphthol (Fig. 3 F) was also observed in organic solvents; acetonitrile and methanol.

Indirect photolysis of carbaryl has been reported by Miller and Chin (2002). They found that photo-enhanced degradation was seasonally and spatially dependent. Nitrate and dissolved organic matter (DOM) were primary constituents responsible for the formation and reaction of hydroxyl radicals with carbaryl (Miller and Chin, 2002).

B. Biotic

1. Microbial

The microbial degradation of carbaryl has been reported in several studies. For instance, ring 14 C-labeled carbaryl degraded at a constant rate in 120 days leaving behind 15-20% of the parent compound in the soil as monitored by the release of 14 C carbon-dioxide (Rodriguez and Dorough, 1977). Shorter degradation times have been observed by Menon and Gopal (2003) that carbaryl dissipated in 45 days (DT₅₀ = 14.93). However, this relatively rapid degradation was attributed to high temperatures and precipitation. Still shorter DT₅₀'s have been reported that ranged from 0.15 (Wolfe et al., 1978) to several days (Tomlin, 2003). In aerobic soils the DT₅₀ was 7-14 days in sandy loam and 14-28 days in clay loam soils (Tomlin, 2003). Bondarenko and Gan (2004) observed aerobic $t_{1/2}$ values of 1.8 and 4.9 days in soils containing 1.8 % (sand:silt:clay = 76:15:9) and 1.25 % (sand:silt:clay = 46:32:22) organic matter, respectively. First-order kinetics described the microbial degradation of carbaryl in most soils (Venkateswarlu et al., 1980). Inhibition of carbaryl can occur when ammonium nitrogen is added to the enrichment cultures (Rajagopal et al., 1983) indicating that nitrogen on the carbamate chain may provide an essential element to microbes.

Degradation has been observed to be more rapid in flooded (anaerobic) soils than aerobic soils; $t_{1/2}$ was 13-14 days in flooded soils while it was 23-28 days in aerobic soils (Venkateswarlu et al., 1980). Rajagopal et al. (1983) observed a DT₅₀ of 10-15 days in submerged laterite and sodic soils. They also observed that degradation was faster in soils previously treated with carbaryl. Recently however, Bondarenko and Gan (2004) reported different findings. Under anaerobic conditions, carbaryl was found to be slowly degraded with $t_{1/2}$ values from 125-746 days depending on soil conditions, sorption capacity, and ageing of the soil with the insecticide.

Fig. 4. Proposed degradation pathway of carbaryl by *Micrococus* sp. (Doddamani and Ninnekar, 2001). Carbaryl (A) is reduced to 1-naphthol and methylamine (B) which is then degraded to salicylic (C) and gentrisic (D) acid. The acids are then oxidized to maleylpyruvate (E).

The mechanisms of degradation have also been reported. Karinen et al. (1967) showed carbaryl ring degradation to CO₂ from 1-naphthol, its primary degradate. Thus, ring structure hydroxylation of carbaryl is the first step in microbial dissipation. Such findings are supported by Rajagopal et al. (1983) where it was noted that hydrolysis at the carbamate bond was the major pathway of degradation in flooded (anaerobic) soils (Fig. 4). The primary degradation product, 1-

naphthol, has a DT₅₀ of approximately 12-14 days (Menon and Gopal, 2003) and can be further transformed to phenolic radicals which polymerize to organic matter in soils (Rajagopal et al., 1984). Complete degradation from carbaryl to maleylpyruvate is reported for an isolated *Micrococcus* species (Fig. 4) by Doddamani and Ninnekar (2001).

Other microbial strains capable of degrading carbaryl have been identified. These include bacterial species *Achromobacter*, *Pseudomonas*, *Arthrobacter*, *Xanthomonas* (Rajagopal, 1984), and *Pseudomonas cepacia* (Venkateswarlu et al., 1980). Degradation by a fungus *Penicillium implicatum* has also been demonstrated (Menon and Gopal, 2003). However, the insecticide has been shown to be inhibitory to the growth of several strains of rhizobia (Rajagopal et al., 1984).

2. Higher-order organisms

The metabolism of carbaryl has been extensively studied and evaluated for mammals. In general, the compound does not accumulate in mammalian tissue and is rapidly metabolized to non-toxic substances, particularly 1-naphthol, which are eliminated in the urine and feces (Tomlin, 2000). The main metabolic pathways in higher-order organisms are hydroxylation, hydrolysis, and expoxidation (Carpenter et al., 1961; Dorough and Casida, 1964). Hydrolysis of carbaryl by earthworms forms 1-naphthol according to Stenersen (1992). A hydrolytic degradation mechanism has been proposed by Sogorb et al. (2002). According to this pathway, carbaryl reacts with tyrosine residues on rabbit serum albumin molecules to yield 1-naphthol and carbamylated rabbit serum albumin. Water molecules than attack the carbamylated complex, releasing carbamic acid and free enzymes, the latter of which is subject to a new catalytic cycle. Carbamic acid is expected to decompose to CO₂ and methylamine (Sogorb et al., 2002).

Metabolites detected in urine of human workers exposed to the carbaryl were 1-naphthyl-glucoronide and 1-naphthylsulphate (Sogorb et al., 2004). Carbaryl metabolism in human liver

microsomes and by cytochrome P450 isoforms was investigated by Tang et al. (2002). They found three major metabolites: 5-hydroxycarbaryl, 4-hydroxycarbaryl, and carbaryl methylol (Fig. 5). Interestingly, these are the same metabolites in plants (Tomlin, 2003).

Fig. 5. The cytochrome P450-dependent metabolism of carbaryl (A) to 4-hydroxycarbaryl, 5-hydroxycarbaryl (C), and (D) carbaryl methylol (Tang et al., 2002).

Factors inhibiting enzymatic carbarylase-driven hydrolysis has also been noted. For instance, data collected by Sogorb et al. (2004) suggest that long chain fatty acids are better inhibitors of carbarylase than shorter ones. Several organic compounds can inhibit carbarylase as well. For example, chlorpyrifos inhibits carbaryl metabolism (Tang et al., 2002) and paraoxon inhibits carbalylase by 44% (Sogorb et al., 2004).

V. Toxicity

Carbaryl is a highly effective insecticide for controlling insect pests. For example, it is used to control several animal ectoparasites, specifically the cattle tick *Boophilus microplus*. This tick is endemic to Mexico, having been eradicated from the U.S. in 1961 according to Li et al.

(2005). Several strains of *B. microplus* were highly susceptible to carbaryl; LC_{50} ranged from 0.0025 to 0.0031% (Li et al., 2005). Carbaryl is highly toxic to the bee at 1 μ g (LD₅₀) topical dose (Tomlin, 2003).

Although carbamate pesticides do not persist in the environment, there may still be short-term cumulative effects on the reproduction of aquatic organisms. For instance, Tripathi and Singh (2004) found that doses of 2, 5, and 8 mg/L carbaryl altered the biochemical parameters in nervous, hepatopancreatic, and ovotesticular tissues of the snail, *Lymnaea acuminate*.

Specifically, glycogen, pyruvate, total protein, and nucleic acid levels were reduced after 96 hours of exposure to carbaryl while lactate and free amino acid levels increased (Tripathi and Singh, 2004). Carbaryl can also affect embryo development. For example, Tripathi and Singh (2004) reported that the number of eggs for the freshwater snail, *Lymnaea acuminate*, were reduced by 49% at 2 mg/L while no eggs were laid at 5 and 8 mg/L. The rate of neonatal survival was also reduced significantly by 53% after exposure of hatchling for 28-day at 2 mg/L. In a similar study Todd and Van Leeuwan (2002) found that the average mortality of zebrafish eggs (*Danio rerio*) was reduced (~20%) after low-level exposures (<0.05 mg/L). Although the insecticide did not directly kill embryos, it had a significant effect on embryo size.

When zebrafish were exposed to 0.017 mg/L of carbaryl, they developed more slowly and hatched later compared to the controls. Delayed hatching exposes zebrafish embryos to predations. The toxicity results of carbaryl to several aquatic animals are summarized in Table 5. Note that carbaryl is toxic to the water flea, shrimp, and freshwater snail at ppb (µg/L) levels while to fish at ppm (mg/L). The results suggest that the insecticide should not be used in bodies of water or in fields adjoining those bodies, particularly in the rainy season.

Table 5. The aquatic animal toxicology of carbaryl.

Aquatic organism	Test	Concentration (mg/L unless noted)
Juvenile trout ^a	96 h LC ₅₀	4.27-6.18
Toad larvae ^a	96 h LC ₅₀	17.68-34.77
Juvenile trout ^a	IC_{50}	19 μg/L
Toad larvae ^a	IC_{50}	7.580
Rainbow trout ^b	96 h LC ₅₀	1.3
Sheephead minnow ^b	96 h LC ₅₀	2.2
Bluegill sunfish ^b	96 h LC ₅₀	10
Mysid shrimp ^b	96 h LC ₅₀	$5.7~\mu \mathrm{g/L}$
Eastern oyster ^b	48 h LC ₅₀	2.7
Shrimp larvae ^c	96 h LC ₅₀	30 μg/L
Common carp ^d	96 h LC ₅₀	7.85
Freshwater snail ^e	24 h LC ₅₀	20.05
Freshwater snail ^e	96 h LC ₅₀	14.19
Water flea (B. longirostris) ^f	24 h LC ₅₀	8.6 μg/L
Water flea (B. fatalis) f	24 h LC ₅₀	4.1 μg/L
Water flea predator (<i>L. kindtii</i>) ^f	24 h LC ₅₀	3.6 µg/L

^a Ferrari et al., 2004; ^b Tomlin, 2003; ^c Reyes et al., 2002; ^d De Mel and Pathiratne, 2005, ^e Tripathi and Singh, 2001; ^f Sakamoto et al., 2005.

Rats and dogs tolerate carbaryl at 200 and 400 mg/kg, respectively (Carpenter et al., 1961). Table 6 summarizers LD₅₀ data of carbaryl to several birds having a greater tolerance to the compound compared to other animals such as rats and dogs.

Table 6. The oral LD $_{50}$ of carbaryl to birds.

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Bird	Concentration (mg/kg)
Mallard duck ^a	>2179
Pheasant ^a	>2000
Japanese quail ^a	2230
Pigeon ^a	1000-3000

^a Tomlin, 2003.

VI. Summary

Carbaryl is an agricultural and garden insecticide that controls a broad spectrum of insects. It is moderately soluble and does not volatilize readily nor easily vaporize. The compound is susceptible to drift after spray application, unstable under alkaline conditions, and easily hydrolyzed. It has been detected in water at µg/L concentrations but degradation of

carbaryl in this environmental medium is relatively rapid with 1-naphthol identified as the major degradation product. Indirect and direct photolysis of carbaryl produces different naphthaquinones as well as some hydroxyl substituted naphthaquinones.

The pesticide's sorption to soil is kinetically fast and both the mineral and organic fractions of soil contribute to its relatively low sorption. Sorption to soil minerals was strongly dependent on the presence of specific exchangeable cations and increased with the soil organic matter aromaticity and age. Microbes in soils (bacteria and fungi) are capable of degrading carbaryl and the process is more rapid in anoxic than aerobic systems and with increased temperature and moisture.

In mammals, the compound does not accumulate and is rapidly metabolized to non-toxic substances which are eliminated in the urine and feces. Several studies have shown that a cumulative effect may exist with respect to the reproduction of aquatic organisms. Therefore, its application near water bodies must be carefully evaluated prior to its use.

VII. References

Ahmad, R., Kookana, R. S., Alston, A. M., Bromilow, R. H. 2001a. Differences in sorption behavior of carbaryl and phosalone in soils from Australia, Pakistan, and the United Kingdom. Aust. J. Soil Res. 39: 893-908.

Ahmad, R., Kookana, R. S., Alston, A. M., Skjemstad, J. O. 2001b. The nature of soil organic matter affects sorption of pesticides. 1. Relationships with carbon chemistry as determined by ¹³C CPMAS NMR spectroscopy. Environ. Sci. Technol. 35: 878-884.

Arroyo, L. J., Li, H., Teppen, B. J., Johnston, C. T., Boyd, S. A. 2004. Hydrolysis of carbaryl by carbonate impurities in reference clay SWy-2. J. Agric. Food Chem. 52: 8066-8073.

Bondarenko, S., Gan, J. 2004. Degradation and sorption of selected organophosphate and carbamate insecticides in urban steam sediments. Environ. Toxicol. Chem. 23: 1809-1814.

Brahmia, O., Richard, C. 2003. Phototransformation of carbaryl in aqueous solution Laser-as photolysis and steady-state studies. J. Photoch. Photobio. A. 156: 9-14.

Carpenter, C. P., Weil, C. S., Palm, P. E., Woodside, M. W., Nair III, J. H., Smyth, H. F. 1961. Mammalian toxicity of 1-naphthyl-N-methylcarbamate (sevin insecticide). J. Agric. Food Chem. 9: 30-39.

CDPR - California Department of Pesticide Regulations (2004) Summary Report; Complete Report with Summary Data Indexed by Chemical. California Environmental Protection Agency, Sacramento, CA pp 340-341. http://www.cdpr.ca.gov/docs/pur/pur04rep/chmrpt04.pdf (verified April 10, 2007).

Cox, C. 1993. The problems with Sevin (carbaryl). J. Pestic. Reform. 13: 31-36.

Currier, W., MacCollom G., Baumann, G. 1982. Drift residues of air-applied carbaryl in an orchard environment. J. Econ. Entomol. 75: 1062-1068.

De Mel, G. M., Pathiratne, A. 2005. Toxicity assessment of insecticides commonly used in rice pest management to the fry of common carp, *Cyprinus carpio*, a food fish culturable in rice fields. J. Appl. Ichthyol. 21: 146-150.

De Oliveira, M. F., Johnston, C. T., Premachandra, G. S., Teppen, B. J., Li, H., Laird, D. A., Zhu, D., Boyd, S. A. 2005. Spectroscopic study of carbaryl sorption on smectite from aqueous suspension. Environ. Sci. Technol. 39: 9123-9129.

Doddamani, H. P., and Ninnekar, H. Z. 2001. Biodegradation of carbaryl by a *micrococcus* species. Curr. Microbiol. 43: 69-73.

Dorough, H. W., Casida, J. H. 1964. Nature of certain carbamate metabolites of the insecticide Sevin. J. Agric. Food Chem. 12: 294-304.

Eichelberger, J. W., Lichtenberg, J. J. 1971. Persistence of pesticides in river water. Environ. Sci. Technol. 5: 541-544.

Ferrari, A., Anguiano, O. L., Venturion, A., Pechen de D'Angelo A. M. 2004. Different susceptibility of two aquatic vertebrates (*Oncorhynchus mykiss* and *Bufo arenarum*) to azinphos methyl and carbaryl. Comp. Biochem. Physiol. 139: 239-243.

Fytianos, K., Pitarakis, K., Bobola, E. 2006. Monitoring of N-methylcarbamate pesticides in the pinios river (central greece) by HPLC. International J. Environ. Anal. Chem. 86: 131-145.

Foreman, W. T., Majewski, M. S., Goolsby, D. A., Wiebe, F. W., Coupe, R. H. 2000. Pesticides in the atmosphere of the Mississippi River Valley, part II – air. Sci. Total Environ. 248: 213-216.

Ghauch, A., Gallet, C., Charef, A., Rima, J., Martin-Bouyer, M. 2001. Reductive degradation of carbaryl in water by zero-valent iron. Chemosphere. 42: 419-424.

Gilliom, R. J., Barbash, J. E., Crawford, C. G., Hamilton, P. A., Martin, J. D., Nakagaki, N., Nowell, L. H., Scott, J. C., Stackelberg, P. E., Thelin, G. P., Wolock, D. M. 2007. The quality of

our nation's waters; pesticides in the nation's streams and groundwater, 1992-2001. U.S. Geological Survey Circular 1291. pp. 52.

Hastings, F. L., Holsten, E. H., Shea, P. J., Werner, R. A. 2001. Carbaryl: a review of its use against bark beetles in coniferous forests of north America. Environ. Entomol. 30: 803-810.

Jana, T., Das, B. 1997. Sorption of Carbaryl (1-Napthyl N-Methyl Carbamate) by Soil. Bull. Environ. Contam. Toxicol. 59:65-71.

Karinen, J. F., Lambertson, J. G., Stewart, N. E., Terrier, L. C. 1967. Persistence of carbaryl in marine estuarine systems. J. Agric. Food Chem. 15: 148.

Kao, A.S. 1994. Formation and removal reactions of hazardous air pollutants. J. Air Waste Manage. 44: 683-96.

LaFleur, K. 1976. Movement of Carbaryl through Congaree Soil into Ground Water. J. Environ. Qual. Vol. 5, No. 1.

Li, A. Y., Davey, R. B., George, J. E. 2005. Carbaryl resistance in Mexican strains of the southern cattle tick (Acari: Ixodidae). J. Econ. Entomol. 98: 552-556.

Martin, J. D., Crawford, C. G., Larson, S. J. 2003. Pesticides in streams – Preliminary results from cycle I of the National Water Quality Assessment Program (NAWQA), 1992-2001. National Water Quality Assessment Program (NAWQA).

Meister, R. T. 2001. Farm Chemicals Handbook. Meister Publishing Company. Willoughby, OH. 88: 83.

Menon, P., Gopal, M. 2003. Dissipation of ¹⁴C carbaryl and quinalphos in soil under a groundnut crop (*Arachis hypogaea* L.) in semi-arid India. Chemosphere. 53: 1023-1031.

Miller, P. L., Chin, Y-P. 2002. Photoinduced degradation of carbaryl in wetland surface water. J. Agric. Food Chem. 50: 6758-6765.

Osman, M., Belal, M. 1980. Persistence of Carbaryl in Canal Water. J. Environ. Sci. Health pt B. 15: 307-311.

Phillips, P. J., Bode, R. W. 2004. Pesticides in surface water runoff in south-eastern New York State, USA: seasonal and stormflow effects on concentrations. Pestic Manag. Sci. 60: 531-543.

Rajagopal, B. S., Brahmaprakash, G. P., Reddy, B. R., Singh, U. D., Sethunathan, N. 1984. Effect and persistence of selected carbamate pesticides in soils. In Reviews of Environmental Contamination and Toxicology. Gunther, F. A., Gunter, J. D. (Eds). Residue Rev. 93: 87-203.

Rajagopal, B. S., Chendrayan, K., Reddy, B. R., Sethunathen, N. 1983. Persistence of carbaryl in flooded soils and its degradation by soil enrichment cultures. Plant Soil. 73: 35-45.

Reyes, J. G. G., Leyva, N. R., Millan, O. A., and Lazcano, G. A. 2002. Effects of pesticides on DNA and protein of shrimp larvae *Litopenaeus stylirostris* of the California gulf. Ecotoxicol. Environ. Saf. 53: 191-195.

Ribera, D., Narbonne, J. F., Arnaud, C., Denis, M. S. 2001. Biochemical responses of the earthworm Eisenia fetida andrei exposed to contaminated artificial soil, effects of carbaryl. Soil Biol. Biochem. 33: 1123-1130.

Rodriguez, L. D., Dorough, H. W. 1977. Degradation of carbaryl by soil microorganisms. Arch. Environ. Contam. Toxicol. 6: 47-56.

Sakamoto, M., Chang, K. H., and Hanazato, T. 2005. Differential sensitive of a predacious cladoceran (*Leptodora*) and its prey (the cladoceren *Bosmina*) to the insecticide carbaryl: results of acute toxicity tests. Bull. Environ. Contam. Toxicol. 75: 28-33.

Sanusi, A., Millet, M., Mirabel, P., Wortham, H. 2000. Comparison of atmospheric pesticide concentrations measured at three sampling sites: local, regional and long-range transport. Sci. Total Environ. 263: 263-277.

Sharom, M. S., Miles, J. R., Harris, C. R., McEwen, F. L. 1980. Behavior of 12 insecticides in soil and aqueous suspensions of soil and sediment. Water Res. 14: 1095-1100.

Shehata T., E. Eichardson and E. Cotton. 1984. Assessment of human population exposure to carbaryl from the 1982 Main Spruce budworm spray project. J. Environ. Health. 46: 293-297.

Sheng, G., Johnston, C. T., Teppen, B. J., and Boyd, S. A. 2001. Potential contributions of smectite clays and organic matter to pesticide retention in soils. J. Agric. Food Chem. 49: 2899-2907.

Sogorb, M. A., Carrera, V., Vilanova, E. 2004. Hydrolysis of carbaryl by human serum albumin. Arch. Toxicol. 78: 629-634.

Sogorb, M. A., Carrera, V., Benabent, M., Vilanova, E. 2002. Rabbit serum albumin hydrolyzes the carbamate carbaryl. Chem. Res. Toxicol. 15: 520-526.

Stenersen, J. Uptake and metabolism of xenobiotics by earthworms. 1992. *In* Ecotoxicology of Earthworms. Greigh-Smith, P. W., Becker, H., Edwards, P. J., Heimbach, F. (Eds.). Intercepts Ltd. Andover, UK. pp. 129-138.

Sun, F., Zhu, T., Shang, I., and Han, L. 2005. Gas-phase reaction of dichlorvos, carbaryl, chlordimeform, and 2,4-D butyl ester with OH radicals. Int. J. Chem. Kinetics. 37: 755-762.

Tang, J., Cao, Y., Rose, R. L., and Hodgson, E. 2002. In vitro metabolism of carbaryl by human cytochrome p450 and its inhibition by chlorpyrifos. Chem. Biol. Interact. 141: 229-241.

Todd, N. E., and Van Leeuwan, M. V. 2002. Effects of sevin (carbaryl insecticide) on early life stages of zebrafish (*Danio rerio*). Ecotoxicol. Environ. Saf. 53: 267-272.

Tomlin, C. D. S. 2003. The Pesticide Manual. 13th Ed. British Crop Protection Council. Surrey, UK. pp. 135-136.

Tomlin, C. D. S. 2000. The Pesticide Manual. 12th Ed. British Crop Protection Council. Surrey, UK. pp. 133-134.

Tripathi, P. K., Singh, A. 2004. Carbaryl induced alteration in the reproduction and metabolism of freshwater snail *Lymnaea acuminata*. Pestic. Biochem. Phys. 79: 1-9.

Tripathi, P. K., Singh, A. 2001. Toxic effects of dimethoate and carbaryl pesticides on carbohydrate metabolism of freshwater snail *Lymnaea acuminate*. B. Environ. Contam. Toxicol. 70: 717-722.

U.S.G.S. (United States Geological Survey) NAWQA data warehouse. 2007. Available at: http://infotrek.er.usgs.gov/traverse/f?p=NAWQA:HOME (verified 24 April, 2007).

Venkateswarlu, K., Chendrayan, K., Sethunathan, N. 1980. Persistence and biodegradation of carbaryl in soils. J. Environ. Sci. Health pt B. 15: 421-429.

Walters, J., Goh, K. S., Li, L., Feng, H., Hernandez, J., and White, J. 2003. Environmental monitoring of carbaryl applied in urban areas to control the glassy-winged sharpshooter in California. Environ. Monit. Assess. 82: 265-280.

Wang Q., Lemley, A. T. 2002. Oxidation of carbaryl in aqueous solution by membrane anodic fenton treatment. J. Agric. Food Chem. 50: 2331-2337.

Ware, G. W. 2000. The Pesticide Manual. Thomson Publications. Fresno, CA. pp. 57, 83, 302.

Whitmore, R.W., Kelly, J.E., Reading, P.L. 1992. Executive summary, results, and recommendations, Volume 1 of National home and garden pesticide use survey, final report. U.S. Environmental Protection Agency, Research Triangle Institute RTI/5100/17-01F. pp. 140.

Wilson, P. C., Foos, J. F. 2006. Survey of carbamate and organophosphorous pesticide export from a south florida (USA) agricultural watershed: implications of sampling frequency on ecological risk estimation. Environ. Toxicol. Chem. 25: 2847-2852.

Wolfe, N. L., Zepp, R. C., Paris, D. F. 1978. Carbaryl, propham, chloropropham: a comparison of rates of hydrolysis and photolysis with the rate of biolysis. Water Res. 12: 565.